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Phase Transformation Introduced by Mechanical and Chemical Surface Preparations of Tetragonal Zirconia Polycrystals

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utting of Y_2O_3-doped TZP rods by a low-speed diamond aw introduces an unidentified, metastable phase X (x-ZrO_2) coexisting with the tetragonal (t-ZrO_2) and the onoclinic (m-ZrO_2) phases initially present in the sample. urther mechanical deformation of the cut surface by ndentation or polishing sustains the x-ZrO_2. Chemical tching removes the x-ZrO_2 and increases the m-ZrO_2 ontent.

I. Introduction

THE phase transformation from tetragonal to monoclinic structure in ZrO_2 can be induced by mechanical stresses[1] nd thermal effects.[2] While there is an established notion that is transformation is martensitic,[3] some recent work on Y-TZP ows that the transformation may be isothermal and bainitic in ature.[4]

Most materials require mechanical and/or chemical surface reparation to render them useful for engineering applications. he present paper reports a preliminary study of the structural hanges brought about by a cutting process and subsequent echanical and chemical treatments of the cut surface.

II. Experimental Procedure

3Y-TZP rods, 5.6 mm in diameter (obtained from M/s CVC cientific Products Ltd., U.K.) were cut by a low-speed saw Buehler, Lake Bluff, IL) incorporated with a 0.3-mm-thick iamond wafering blade, under a load of 2 N at 175 rpm using n oil-based lubricant. The cut surfaces were subjected to three ifferent treatments: (i) polishing—using a 3-μm diamond aste; (ii) indentation—21 indents of 70-μm depth made using 120° included angle cone indenter, and (iii) etching—in boiling orthophosphoric acid for 0.75, 2, and 3 min.

X-ray diffraction (XRD) patterns were recorded using Cu$K\alpha$ adiation in powder diffractometer with a monochromator in the iffracted beam and a proportional counter. Sample rotation peed and the chart speed were 1/4° and 10 mm/min, respectively. For profile fitting, point-counted intensity data were collected at 2θ intervals of 0.02°.

III. Results and Discussion

Figure 1(A) shows part of the XRD pattern recorded from the irgin surface of an as-received 3Y-TZP rod. The sample is redominantly tetragonal. The presence of a small fraction of m-ZrO_2 is revealed by the occurrence of reflections at $2\theta \approx$ 28.5° and 31.5°. The volume fraction of the monoclinic phase, v_M, estimated from the relation[5]

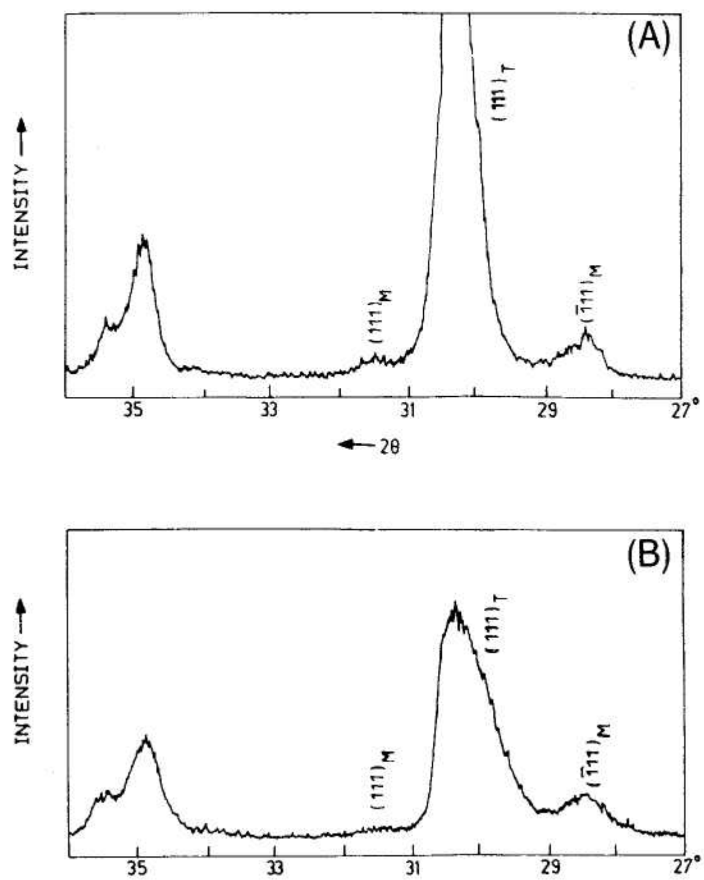
$$v_M = \frac{I(\bar{1}11)_M + I(111)_M}{I(\bar{1}11)_M + I(111)_M + I(111)_T} \qquad (1)$$

is ~0.2. In Eq. (1) the $I(hkl)$'s represent the integrated intensities, I_{obs}, corrected for Lorentz polarization (Lp), multiplicity (m), and thermal vibrations (B), and normalized with respect to Σf_j^2, where the f_j's correspond to the atomic scattering factors of the zirconium and the oxygen atoms:

$$I(\mathrm{hkl}) = I_{obs}\frac{1}{\mathrm{Lp}}\frac{1}{m}\frac{1}{\Sigma f_j^2 e^{-2B\sin^2\theta/\lambda^2}} \qquad (2)$$

The temperature factors B_{Zr} and B_O used in Eq. (2) are 1.66 and 3.11 Å^2, respectively.[6] θ and λ correspond to the Bragg angle of the reflection (hkl) and the wavelength of the radiation, respectively.

Cutting of the rods introduces a shoulder (Fig. 1(B)) on the low-angle side of the most intense t-ZrO_2 reflection, $(111)_T$. Least-squares fitting of a split-Pearson function to the asymmetric profile clearly shows (Fig. 2) that the shoulder is due to the



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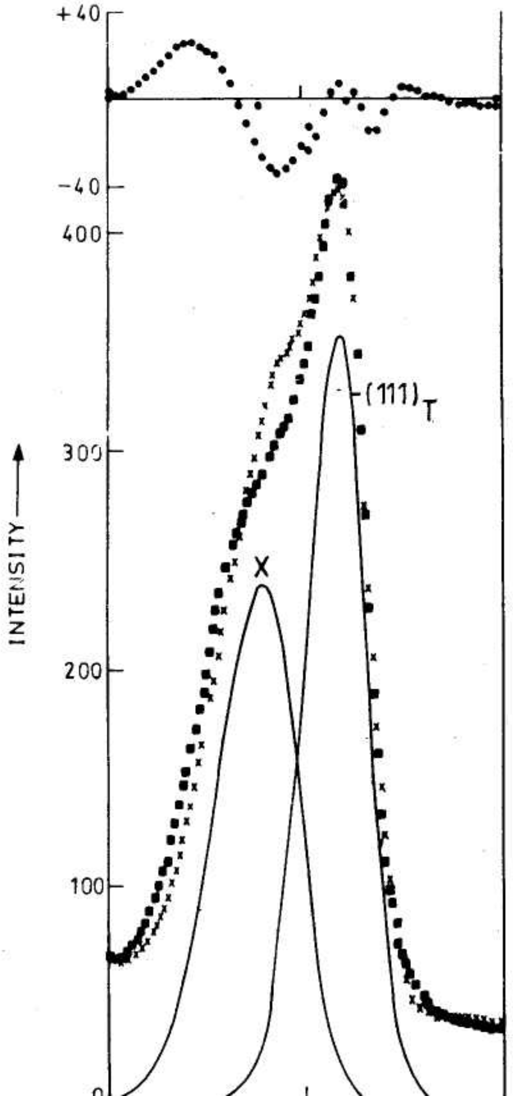
introduction of a new reflection, partially overlapping with $(111)_T$ on the low-angle side. The new reflection at $2\theta = 29.8°$ ($d = 0.300$ nm) is distinct and does not match with the available XRD data on the t-ZrO_2, m-ZrO_2, or o-ZrO_2 phases.[7-9] We therefore attribute it to a new phase X (x-ZrO_2). XRD patterns beyond $2\theta = 30°$ do not lead to an unambiguous identification of this phase or clarify the existence of any long-range order. The observed 2θ value of the new reflection is, however, closer to $(111)_T$ than to $(\bar{1}11)_M$. This feature suggests the possibility of the x-ZrO_2 phase being intermediate in structure between t-ZrO_2 and m-ZrO_2. Further, the serrated appearance of the shoulder in Fig. 1(B) suggests that x-ZrO_2 may be characterized by varying concentrations of crystallographic planes with slightly differing d-values. Thus the x-ZrO_2 phase appears to be ill-defined.

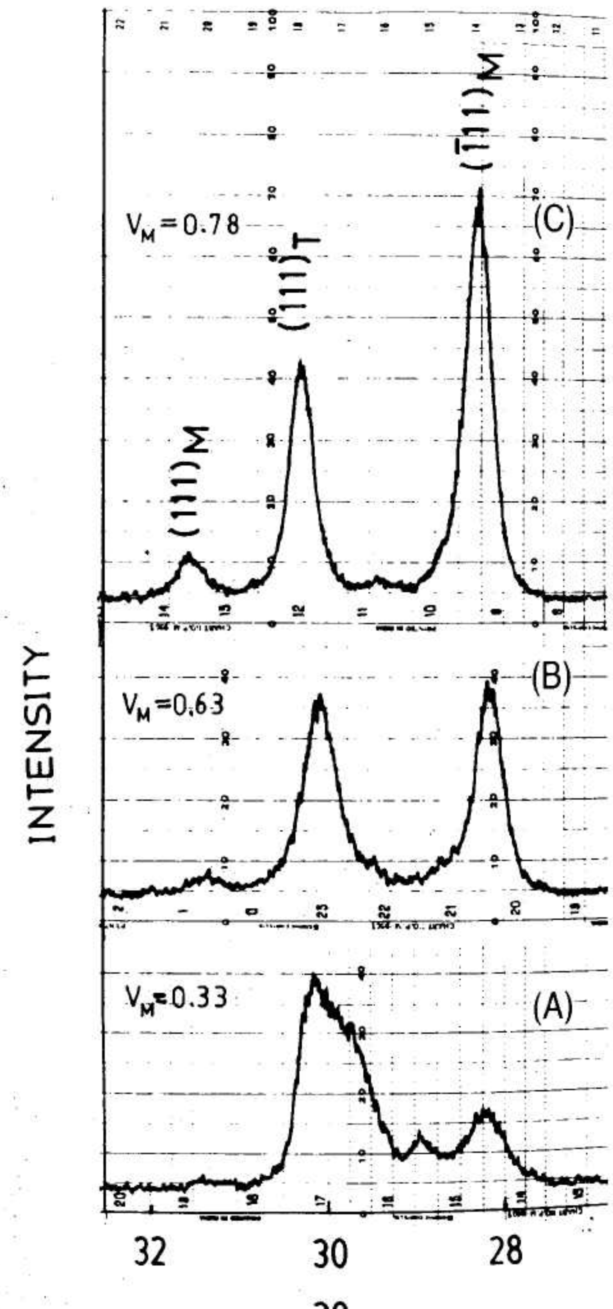
It is interesting to note that another mechanical process, indentation, which involves high hydrostatic stresses, induces the $t \rightarrow m$ transformation in TZP.[10] Cutting, in contrast, induces stresses which have a large shear component. The present evidence therefore suggests that the $t \rightarrow x$ transformation is favored by shear stresses.

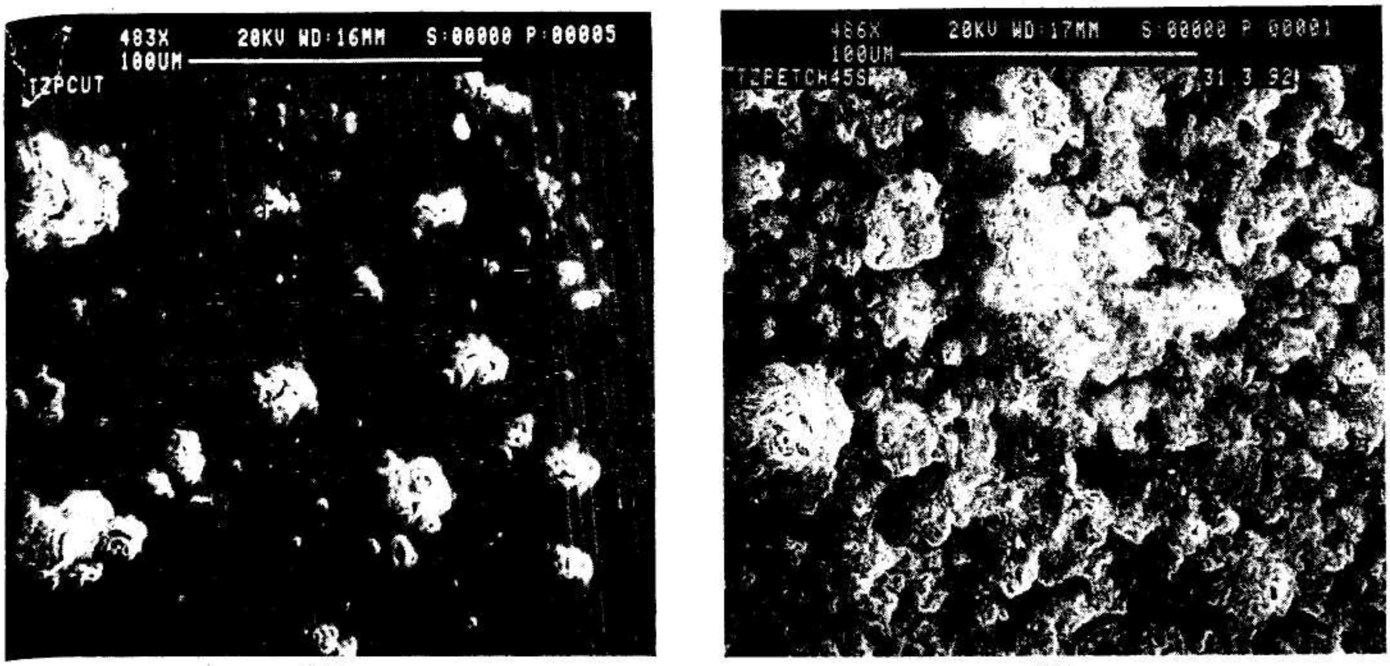
XRD data from cut and etched samples (Figs. 3(A), (B), and (C)) show that etching reduces the amount of x-ZrO_2 and increases the m-ZrO_2 content. The gradual decrease in the amount of x-ZrO_2 and increase in the amount of m-ZrO_2 with etching time may be due to the layer-by-layer removal of x-ZrO_2 and the increasing exposure of the underlying t-ZrO_2 to the acid, leading to $t \rightarrow m$ transformation. Etching with hot sulfuric acid is known to induce the $t \rightarrow m$ transformation.[11] It is also possible, as suggested by the coexistence of x-ZrO_2 and m-ZrO_2 on the lightly etched cut surface (Fig. 3(A)), that the x-ZrO_2 is transforming directly to m-ZrO_2. This issue is not yet resolved.

Scanning electron micrographs of the cut surface (Fig. 4(A)) show parallel cutting marks interrupted by pits. The pits may be due to pull-out of transformed grains during cutting.[9] As cutting does not induce any significant amount of $t \rightarrow m$ transformation (compare Figs. 1(A) and (B)), the pits (Fig. 4(A)) may be pockets where $t \rightarrow x$ transformation has occurred. Figure 4(B) shows the pits on the cut surface to become more numerous with etching. After prolonged (3-min) etching, these pits merge with each other to yield a granular surface. Thus, the morphology of the surface suggests that regardless of whether the transformation is $t \rightarrow x$ or $t \rightarrow m$, the associated feature is pitting due to the localized volume changes.

When a cut surface containing x-ZrO_2 is indented, the phase assemblage does not change significantly. Polishing the cut surface also did not induce either $t \rightarrow m$ or $x \rightarrow m$ transformation. Srinivasan *et al.*[12] report the inhibition of $t \rightarrow m$ transformation induced by the presence of sulfate ions on the surface. In this study, the x-ZrO_2 phase may play a similar role.







(A) (B)

Fig. 4. Scanning electron micrographs of (A) cut surface (B) cut surface etched for 45 s.

IV. Conclusions

Commercial 3Y-TZP rods containing $\approx 20\%$ m-ZrO_2 were it using a low-speed diamond saw. Cutting introduces a new -ray reflection with $d = 0.300$ nm, proposed to arise from an nidentified polymorph, x-ZrO_2. Indenting or polishing the cut irface sustains the x-ZrO_2 phase without any significant icrease in the monoclinic volume fraction v_M. Thus, the ZrO_2 seems to act as a barrier to further transformation of the ZP. However, with etching, the x-ZrO_2 phase disappears, with simultaneous increase in m-ZrO_2 content.

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